

APPLICATION FOR UNITED STATES LETTERS PATENT

for

BIODEGRADABLE SURFACTANT FOR  
INVERT EMULSION DRILLING FLUID

by

Arvind D. Patel

Burnhan Hoxha

and

Reginald Bell

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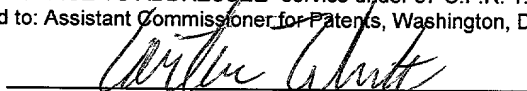
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## BACKGROUND OF THE INVENTION

In rotary drilling of subterranean wells numerous functions and characteristics are expected of a drilling fluid. A drilling fluid should circulate throughout the well and carry cuttings from beneath the bit, transport the cuttings up the annulus, and allow their separation at the surface. At the same time, the drilling fluid is expected to cool and clean the drill bit, reduce friction between the drill string and the sides of the hole, and maintain stability in the borehole's uncased sections. The drilling fluid should also form a thin, low permeability filter cake that seals openings in formations penetrated by the bit and act to reduce the unwanted influx of formation fluids from permeable rocks.

Drilling fluids are typically classified according to their base material. In oil base fluids, solid particles are suspended in oil, and water or brine may be emulsified with the oil. The oil is typically the continuous phase. In water base fluids, solid particles are suspended in water or brine, and oil may be emulsified in the water. The water is typically the continuous phase. Pneumatic fluids are a third class of drilling fluids in which a high velocity stream of air or natural gas removes drill cuttings.

Invert emulsion fluids, i.e. emulsions in which the non-oleaginous fluid is the discontinuous phase and the oleaginous fluid is the continuous phase, are employed in drilling processes for the development of oil or gas sources, as well as, in geothermal drilling, water drilling, geoscientific drilling and mine drilling. Specifically, the invert emulsion fluids are conventionally utilized for such purposes as providing stability to the drilled hole, forming a thin filter cake, lubricating the drilling bore and the downhole area and assembly, and penetrating salt beds without sloughing or enlargement of the drilled hole.

Oil-based drilling fluids are generally used in the form of invert emulsion muds. An invert emulsion mud consists of three-phases: an oleaginous phase, a non-oleaginous phase and a finely divided particle phase. Also typically included are emulsifiers and emulsifier systems, weighting agents, fluid loss additives, viscosity regulators and the like, for stabilizing the system as a whole and for establishing the desired performance properties. Full particulars can be found, for example, in the article by P. A. Boyd et al entitled "New Base Oil Used in Low-Toxicity Oil Muds" in the Journal of Petroleum

Technology, 1985, 137 to 142 and in the Article by R. B. Bennet entitled "New Drilling Fluid Technology-Mineral Oil Mud" in Journal of Petroleum Technology, 1984, 975 to 981 and the literature cited therein. Also reference is made to the description of invert emulsions found in Composition and Properties of Drilling and Completion Fluids, 5th Edition, H. C. H. Darley, George R. Gray, Gulf Publishing Company, 1988, pp. 328-332, the contents of which are hereby incorporated by reference.

The emulsifying agent component of the invert emulsion drilling fluid serves to lower the interfacial tension of the liquids so that the non-oleaginous liquid may form a stable dispersion of fine droplets in the oleaginous liquid. As used herein, emulsifying agent and surfactant are used interchangeably. Typically emulsifying agents are chemical compounds that are polar on one portion of the molecule and non-polar on another area. Such characteristics allow the emulsifying agent to be slightly soluble in both the oleaginous phase and the non-oleaginous phase and thus found at the interfacial surfaces between the two. Because of the unique characteristics of such compounds, the biodegradability is limited. In some cases, the surfactant molecules are toxic to the biodegrading organism.

As a result of the above, there remains and exists an unmet need for a surfactant package that can be used to formulate invert emulsion drilling fluids and yet remain biodegradable.

## SUMMARY OF THE INVENTION

The present invention is generally directed to an invert emulsion drilling fluid that is formulated using a biodegradable surfactant. As disclosed below, such a fluid includes: an oleaginous continuous phase, a non-oleaginous discontinuous phase, a surfactant that is a fatty acid ester of diglycerol or triglycerol, and a weighting agent. In one such illustrative embodiment, the surfactant is a di-fatty acid ester of diglycerol in which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and R is an alkyl or akenyl having 10 to 20 carbon atoms. Alternatively, the surfactant is a di-fatty acid ester of triglycerol in which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and the R is an alkyl or akenyl having 10 to 20 carbon atoms. More preferably the surfactant is selected from polyglyceryl-2

1 diisostearate or polyglyceryl-3 diisostearate or mixtures and combinations of these. One  
2 of skill in the art should appreciate that the oleaginous fluid may be selected from a wide  
3 variety of suitable materials. Examples include: diesel oil, mineral oil, synthetic oil, ester  
4 oils, glycerides of fatty acids, aliphatic esters, aliphatic ethers, aliphatic acetals, or other  
5 such hydrocarbons and combinations and mixtures of these and similar fluids. In a  
6 similar manner, the non-oleaginous phase may be selected from a wide variety of suitable  
7 materials. Examples of which include: fresh water, sea water, brine, aqueous solutions  
8 containing water soluble organic salts, water soluble alcohols or water soluble glycols or  
9 combinations and mixtures of these and similar fluids. The weighting agent component  
10 of such an illustrative drilling fluid can be either a water-soluble weighting agent or a  
11 water insoluble weighting agent or combinations and mixtures of these two. In one  
12 illustrative embodiment, the water insoluble weighting agent is selected from barite,  
13 calcite, mullite, gallena, manganese oxides, iron oxides, or combinations and mixtures of  
14 these and similar solid materials used to weight drilling fluids. In another illustrative  
15 embodiment, the water soluble weighting agent is selected from water soluble salts of  
16 zinc, iron, barium, calcium or combinations and mixtures of these in aqueous solutions  
17 used to add weight to drilling fluids.

18 Also encompassed by the present invention are the methods of formulating such  
19 fluids and using such fluids in the drilling of subterranean wells. For example in one such  
20 embodiment, a drilling fluid as described below is formulated, circulated in a rotary  
21 drilling drill string and utilized as the drilling fluid in drilling a well.

22 These and other features of the present invention are more fully set forth in the  
23 following description of preferred or illustrative embodiments of the invention.

## 24 **DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS**

25 The present invention is generally directed to invert emulsion drilling fluids and  
26 their use in the drilling of subterranean wells. The invert emulsion fluids of the present  
27 invention generally are composed of an oleaginous continuous phase, a non-oleaginous  
28 discontinuous phase, a surfactant that is a fatty acid ester of diglycerol or triglycerol, and  
29 a weighting agent.  
30

As used herein the term "oleaginous liquid" means oil which is a liquid at 25°C and immiscible with water. Oleaginous liquids typically include substances such as diesel oil, mineral oil, synthetic oil such as polyolefins or isomerized polyolefins, ester oils, glycerides of fatty acids, aliphatic esters, aliphatic ethers, aliphatic acetals, or other such hydrocarbons and combinations of these fluids. In one illustrative embodiment of this invention the oleaginous liquid is an polyolefin material which provides environmental degradability to the overall drilling fluid. Such polyolefins should be selected such that the molecular weight permits for a functional invert emulsion drilling fluid to be formulated. Especially preferred are isomerized polyolefins having a carbon backbone of 16 to 18 carbons and in which at least one point of unsturation is internal.

The amount of oleaginous liquid in the invert emulsion fluid may vary depending upon the particular oleaginous fluid used, the particular non-oleaginous fluid used, and the particular application in which the invert emulsion fluid is to be employed. However, generally the amount of oleaginous liquid must be sufficient to form a stable emulsion when utilized as the continuous phase. Typically, the amount of oleaginous liquid is at least about 30, preferably at least about 40, more preferably at least about 50 percent by volume of the total fluid.

As used herein, the term "non-oleaginous liquid" mean any substance which is a liquid at 25°C and which is not an oleaginous liquid as defined above. Non-oleaginous liquids are immiscible with oleaginous liquids but capable of forming emulsions therewith. Typical non-oleaginous liquids include aqueous substances such as fresh water, seawater, brine containing inorganic or organic dissolved salts, aqueous solutions containing water-miscible organic compounds and mixtures of these. In one illustrative embodiment the non-oleaginous fluid is brine solution including inorganic salts such as calcium halide salts, zinc halide salts, alkali metal halide salts and the like.

The amount of non-oleaginous liquid in the invert emulsion fluid may vary depending upon the particular non-oleaginous fluid used and the particular application in which the invert emulsion fluid is to be employed. Typically, the amount of non-oleaginous liquid is at least about 1, preferably at least about 3, more preferably at least about 5 percent by volume of the total fluid. Correspondingly, the amount should not be

so great that it cannot be dispersed in the oleaginous phase. Therefore, typically the amount of non-oleaginous liquid is less than about 90, preferably less than about 80, more preferably less than about 70 percent by volume of the total fluid.

As the term is used herein, "surfactant" and "emulsifier" or "emulsifying agent" are used interchangeably to indicate that component of the invert emulsion drilling fluid that stabilizes the invert emulsion. One of ordinary skill in the art should appreciate that such a compound acts at the interface of the oleaginous and the non-oleaginous fluids and lowers the differences in surface tension between the two layers. In the present invention it is important that the emulsifying agent does not adversely affect the biodegradability of the invert emulsion. The ability of any particular emulsifying agent to stabilize the invert emulsion can be tested by using the invert emulsion test disclosed below. In addition if the emulsifying agent is to be useful in the formulation of a drilling fluid, the emulsifier should be thermally stable. That is to say, the emulsifier must not break down or chemically degrade upon heating to temperatures typically found in a downhole environment. This may be tested by heat aging the emulsifier as is done in the Examples.

Typically prior art emulsion compounds are difficult or are very slow to biodegrade. However, it has been found that fatty acid esters of diglycerol or triglycerol function as surfactants that are readily biodegradable. In one preferred embodiment of the present invention, the surfactant is a di-fatty acid ester of diglycerol in which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and the R is an alkyl or akenyl having 10 to 20 carbon atoms. Alternatively, the surfactant is a di-fatty acid ester of triglycerol in which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and the R is an alkyl or akenyl having 10 to 20 carbon atoms. As illustrated in the examples below, it is especially preferred that the surfactant is a polyglyceryl-2 diisostearate or polyglyceryl-3 diisostearate or mixtures of these. A suitable emulsifier within the scope of the present invention should be capable of stabilizing the invert emulsion under conditions of heat aging. The amount of the emulsifier needed to form a stable invert emulsion can be determined by systematically adjusting the amount of emulsifier added and testing the stability of the fluid. Preferably the amount of emulsifier should be from about 1 to about 20 pounds per barrel (ppb) and more preferably from about 8 to about 12 ppb of the drilling fluid.

The invert emulsion drilling fluids preferably contain weight materials. The quantity and nature of the weight material depends upon the desired density and viscosity of the final composition. The preferred weight materials include, but are not limited to, barite, calcite, mullite, gallena, manganese oxides, iron oxides, mixtures of these and the like. The weight material is typically added in order to obtain a drilling fluid density of less than about 24, preferably less than about 21, and most preferably less than about 19.5 pounds per gallon.

Viscosifying agents, for example, organophillic clays, may optionally be employed in the invert drilling fluid compositions of the present invention. Usually, other viscosifying agents, such as oil soluble polymers, polyamide resins, polycarboxylic acids and fatty acid soaps may also be employed. The amount of viscosifying agent used in the composition will necessarily vary depending upon the end use of the composition. Usually such viscosifying agents are employed in an amount which is at least about 0.1, preferably at least about 2, more preferably at least about 5 percent by weight to volume of the total fluid. VG-69™ and VG-PLUS™ are organoclay materials and Versa HRP™ is a polyamide resin material manufactured and distributed by M-I L.L.C. which are suitable viscosifying agents.

Fluid loss control agents such as modified lignite, polymers, oxidized asphalt and gilsonite may also be added to the invert drilling fluids of this invention. Usually such fluid loss control agents are employed in an amount, which is at least about 0.1, preferably at least about 1, more preferably at least about 5 percent, by weight to volume of the total fluid.

One skilled in the art may readily identify using the following test if he has used the appropriate ingredients and amounts to form an invert emulsion:

INVERT EMULSION TEST: A small portion of the emulsion is placed in a beaker which contains an oleaginous fluid. If the emulsion is an invert emulsion, the small portion of the emulsion will disperse in the oleaginous fluid. Visual inspection will determine if it has so dispersed.

Alternatively, the electrical stability of the invert emulsion may be tested using a typical emulsion stability tester. Generally the voltage applied across two electrodes is

increased until the emulsion breaks and a surge of current flows between the two electrodes. The voltage required to break the emulsion is a common measure of the stability of such an emulsion. Other tests are described on page 166 of the book, Composition and Properties of Drilling and Completion Fluids, 5th Edition, H. C. H. Darley and George Gray, Gulf Publishing Company, 1988, the contents of which are hereby incorporated by reference.

The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the invention.

The following examples are submitted for the purpose of illustrating the performance characteristics of the drilling fluid compositions of this invention. These tests were conducted substantially in accordance with the procedures in API Bulletin RP 13B-2, 1990 which is incorporated herein by reference. The following abbreviations may be used in describing the results of experimentation:

“E.S.” is electrical stability of the emulsion as measured by the test described in Composition and Properties of Drilling and Completion Fluids, 5th Edition, H. C. H. Darley, George R. Gray, Gulf Publishing Company, 1988, pp. 116, the contents of which are hereby incorporated by reference. Generally, the higher the number, the more stable the emulsion.

“PV” is plastic viscosity that is one variable used in the calculation of viscosity characteristics of a drilling fluid, measured in centipoise (cP) units.

“YP” is yield point that is another variable used in the calculation of viscosity characteristics of drilling fluids, measured in pounds per 100 square feet (lb/100ft<sup>2</sup>).

“AV” is apparent viscosity that is another variable used in the calculation of viscosity characteristic of drilling fluid, measured in centipoise (cP) units.



“GELS” is a measure of the suspending characteristics, or the thixotropic properties of a drilling fluid, measured in pounds per 100 square feet (lb/100 ft<sup>2</sup>).

“API F.L.” is the term used for API filtrate loss in milliliters (ml).

“HTHP” is the term used for high temperature high pressure fluid loss at 200°F, measured in milliliters (ml) according to API bulletin RP 13 B-2, 1990.

As used in the formulation of the drilling fluids illustrated in the following example the following component names are intended to mean the following:

IO C<sub>16-18</sub> is a isomerized olefin used as a synthetic based drilling fluid available commercially as Amodril-1000 from Amoco Co.

Bio Base-300 is a mixture of blended linear parafin (93%) and olefin available commercially from Shrieve Chemicals Co.

BENTONE 38 is an organophillic clay viscosifying agent available commercially from M-I LLC of Houston, Texas.

MI Bar is a barite based weighting agent available commercially from M-I LLC of Houston Texas.

Emulpharma PG20 is a emulsifier available commercially from RES Pharma of Italy.

VERSAWET is a wetting agent available commercially from M-I LLC of Houston Texas.

VERSAVERT F is a fluid loss control agent available commercially from M-I LLC of Houston Texas.

VERSA SWA is a wetting agent available commercially from M-I LLC of Houston Texas.

VERSAMOD is a LSRV agent available commercially from M-I LLC of Houston Texas.

BENTONE (EMI 155), is a viscosifier available from M-I LLC of Houston Texas..

ARM 1-73A is a choline chloride emulsifier available commercially from Special Product Co. of Houston, Texas.

Ecotrol (EMI-526) is a fluid loss control agent available commercially from M-I LLC of Houston, Texas

VG PLUS is a viscosifier available commercially from M-I LLC of Houston Texas.

NOVA PLUS is a synthetic mud system available commercially from M-I LLC of Houston Texas.

NOVAMUL is a emulsifying agent used with the NOVA PLUS system available commercially from M-I LLC of Houston Texas.

NOVAWET is a wetting agent used with the NOVA PLUS system available commercially from M-I LLC of Houston Texas.

VERSACOAT is a primary emulsifying agent available commercially from M-I LLC of Houston Texas.

Lime is commercially acceptable grade of calcium hydroxide commonly available.

$\text{CaCl}_2$  (95%), is an aqueous calcium chloride solution having 95% by weight calcium choride.

REV DUST is a simulated drill cuttings material available from M-I LLC of Houston, Texas.

Class G Cement is a Portland cement formulated for use in cementing subterranean wells that is commercially available.

Zechstein brine is an aqueous brine solution containing 50% w/v magnesium chloride, 0.038 w/v potassium chloride; 0.026 w/v sodium chloride; 0.63 v/v deionized water.

All values associated with the formulations described below are grams unless otherwise specified.

#### Example 1. Drilling Fluid with 25% $\text{CaCl}_2$ Brine

A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	A
IO C <sub>16-18</sub> , g	173.7
BENTONE 38, g	7.0
Lime, g	2.0
Emulpharma PG20, g	8.0
Tapwater, g	54.3
CaCl <sub>2</sub> (95%), g	18.1
CaCO <sub>3</sub> , g	35
MI Bar, g	208.9

The formulated fluid had a mud weight of about 11.8 ppg. The initial properties of the fluid were measured and then the fluid was aged at 200 °F for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F. Representative data is given below:

Fluid Properties	Initial	Aged
600 rpm Rheology	65	73
300 rpm Rheology	42	49
200 rpm Rheology	32	37
100 rpm Rheology	23	24
6 rpm Rheology	11	4
3 rpm Rheology	9	3
PV., cP	23	24
YP, lb/100 Ft <sup>2</sup>	19	25
10 s. Gel, lb/100 ft <sup>2</sup>	11	3
10 min, Gel, lb/100 t <sup>2</sup>	13	8
HTHP @ 250°F, cc/30	8	0.8
ES @ 120°F, Volts	267	609

The ability of the above fluid to withstand contamination was tested by adding Zechstein (43 g) or a slurry of class G cement (70g) to the initial unaged drilling fluid. After aging the fluid . The fluid mixture was aged at 200 °F for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F. Representative data is given below:

Fluid Properties	Zechstein (43 g)	Class G Cement (70g slurry)
600 rpm Rheology	59	85
300 rpm Rheology	37	59
200 rpm Rheology	28	36
100 rpm Rheology	19	22
6 rpm Rheology	8	4
3 rpm Rheology	6	3
PV., cP	22	26
YP, lb/100 Ft <sup>2</sup>	15	33
10 s. Gel, lb/100 ft <sup>2</sup>	8	4
10 min, Gel, lb/100 t <sup>2</sup>	11	11
HTHP @ 250°F, cc/30	3.6	1.4
ES @ 120°F, Volts	439	305

Upon review of the above data, one of ordinary skill in the art should appreciate that the above formulated fluid is useful as an invert emulsion drilling fluid. Further, the fluid retains the properties required of a drilling fluid upon contamination by simulated contamination by Zechstein or a slurry of Class G cement.

#### Example 2. Drilling Fluid with 25% CaCl<sub>2</sub> Brine

A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	B
Bio Base-300, g	173.4
BENTONE 38, g	9.0
Lime, g	2.0
Emulpharma PG20, g	8.0
VERSAWET, g	1.0
Tapwater, g	54.3
CaCl <sub>2</sub> (95%), g	18.1
CaCO <sub>3</sub> , g	35
MI Bar, g	208.9

The formulated fluid had a mud weight of about 11.8 ppg. The initial properties of the fluid were measured and then the fluid was aged. Rheology of the initial fluid and the aged fluid were measured at 120 °F. The ability of the above fluid to withstand contamination was tested by adding a slurry of class G cement (70g) or REV DUST (50g)

to the initial unaged drilling fluid. The fluid mixture was aged at 200 °F for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F. Representative data is given below:

Class G Cement % v/v	10(70g slurry)	
REV DUST, % w/w		5(50 g)
Fluid Properties	Aged	Aged
600 rpm	119	41
300	78	24
200	60	15
100	42	10
6	17	3
3	15	2
PV., cP	41	17
YP, lb/100 Ft <sup>2</sup>	37	7
10 s. Gel, lb/100 ft <sup>2</sup>	17	2
10 min, Gel, lb/100 t <sup>2</sup>	19	6
HTHP @ 250°F, cc/30	8.6	1.0
ES @ 120°F, Volts	126	170

Upon review of the above data, one of ordinary skill in the art should appreciate that the above formulated fluid is useful as an invert emulsion drilling fluid. Further, the fluid retains the properties required of a drilling fluid upon contamination by simulated contamination by a slurry of Class G cement or Rev Dust as a simulated drilling cuttings solid.

### Example 3. Drilling Fluid with 25% CaCl<sub>2</sub> Brine

A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	C	D	E	F	G
Bio Base	173.7	173.7	173.7	173.7	173.7
BENTONE 38, g	-	9.0	-	12.0	9.0
BENTONE (EMI 155), g	9.0	-	9.0	-	-
Lime, g	2.0	2.0	2.0	2.0	2.0
Emulpharma PG20, g	-	10.0	10.0	10.0	10.0
ARM 1-73A, g	13.0	-	-	-	-
VERSAWET g	1.0	1.0	1.0	1.0	1.0
Ecotrol					0.5
Tap water, g	54.3	54.3	54.3	54.3	54.3
CaCl <sub>2</sub> (25%), g	18.1	18.1	18.1	18.1	18.1
CaCO <sub>3</sub> , g	35	35	35	35	35
MI Bar, g	208.9	208.9	208.9	208.9	208.9

The formulated fluid had a mud weight of about 11.8 ppg. The initial properties of the fluid were measured and then the fluid was aged at the temperatures shown for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F. Representative data is given below:

Fluid Formulation	C		D	
Fluid Properties	Initial	Aged	Initial	Aged
Aged Temp °F		200		300
600 rpm Rheology	Too thick to measure		45	Too thick to measure
300 rpm Rheology			30	
200 rpm Rheology			20	
100 rpm Rheology			14	
6 rpm Rheology			6	
3 rpm Rheology			5	
PV., cP			15	
YP, lb/100 Ft <sup>2</sup>			15	
10 s.Gel, lb/100 ft+			6	
10 min,Gel,lb/100 t <sup>2</sup>			9	
HTHP@250°F, cc/30			-	
ES @ 120°F, Volts			775	

Fluid Formulation	E		F		G	
Fluid Properties	Initial	Aged	Initial	Aged	Initial	Aged
Aged Temp °F		250		300		300
600 rpm Rheology	65	56	61	44	43	138
300 rpm Rheology	44	31	42	25	30	100
200 rpm Rheology	33	20	33	18	20	83
100 rpm Rheology	25	11	25	10	15	60
6 rpm Rheology	12	3	12	3	7	12
3 rpm Rheology	11	2	11	2	6	10
PV., cP	11	25	19	19	13	38
YP, lb/100 Ft <sup>2</sup>	22	6	23	6	17	62
10 s.Gel, lb/100 ft+	12	2	12	2	7	8
10 min,Gel,lb/100 t <sup>2</sup>	14	6	15	3	9	11
HTHP@250°F, cc/30	-	4.4	-	10	-	5.6
ES @ 120°F, Volts	649	471	617	325	711	388

Upon review of the above data, one of ordinary skill in the art should appreciate that the above-formulated fluids are useful as an invert emulsion drilling fluids. Further, in formulation D the mud was too thick to measure after aging. In formulations E & F light senerises effect was observed.

#### Example 4. Drilling Fluid with 25% CaCl<sub>2</sub> Brine

A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	H	I	J	K	L
Bio Base-300, g	173.7	173.7	173.7	173.7	173.7
BENTONE 38, g	12.0	-	7.0	9.0	12.0
BENTONE (EMI 155), g	-	9.0	-	-	-
Lime, g	2	2	2	2	2
Emulpharma PG20, g	10.0	10.0	10.0	10.0	10.0
VERSAWET, g	1.0	1.0	1.0	1.0	1.0
Ecotrol(EMI-526), g	0.5		0.5	0.25-	-
Tap water, g	54.3	54.3	54.3	54.3	54.3
CaCl <sub>2</sub> (95%), g	18.1	18.1	18.1	18.1	18.1
CaCO <sub>3</sub> , g	35	35	35	35	35
MI Bar, g	208.9	208.9	208.9	208.9	208.9

The formulated fluid had a mud weight of about 11.8 ppg. The initial properties of the fluid were measured and then the fluid was aged at 300 °F shown for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F. Representative data is given below:

Fluid Formulation	H		I		J	
Fluid Properties	Initial	Aged	Initial	Aged	Initial	Aged
600 rpm Rheologies	60	138	64	47	34	86
300 rpm Rheologies	42	92	42	27	22	58
200 rpm Rheologies	32	79	32	19	16	45
100 rpm Rheologies	24	53	24	12	11	32
6 rpm Rheologies	12	15	12	4	6	12
3 rpm Rheologies	11	12	10	2	5	10
PV., cP	18	46	22	20	12	28
YP, lb/100 Ft <sup>2</sup>	24	46	20	7	10	30
10 s. Gel, lb/100 ft <sup>2</sup>	11	13	10	4	6	12
10 min, Gel, lb/100 t <sup>2</sup>	14	16	12	6	8	14
HTHP @ 250°F, cc/30	-	5.6	-	9.2	-	5.2
ES @ 120°F, Volts	791	421	673	198	626	522

Fluid Formulation	K		L
Fluid Properties	Initial	Aged	Aged
600 rpm Rheologies	45	60	154
300 rpm Rheologies	31	35	110
200 rpm Rheologies	23	26	91
100 rpm Rheologies	16	16	68
6 rpm Rheologies	8	4	28
3 rpm Rheologies	7	2	25
PV., cP	14	25	44
YP, lb/100 Ft <sup>2</sup>	17	10	66
10 s. Gel, lb/100 ft <sup>2</sup>	8	3	22
10 min, Gel, lb/100 t <sup>2</sup>	11	4	26
HTHP @ 250°F, cc/30	-	5.0	14.0
ES @ 120°F, Volts	710	361	252

Upon review of the above data, one of ordinary skill in the art should appreciate that the above-formulated fluids are useful as an invert emulsion drilling fluids.



1 Example 5. Drilling Fluid with 25% CaCl<sub>2</sub> Brine

2 A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	M	N	O	P	Q
Bio Base-300, g	173.7	173.7	173.7	173.7	173.7
BENTONE 38, g	7.0	7.0	7.0	7.0	7.0
Lime, g	2	2	2	2	2
Emulphama PG20, g	10.0	10.0	10.0	10.0	10.0
VERSAWET, g	1.0	3.0	-	-	-
VERSA SWA, g	-	-	0.5	0.5	1.0
Ecotrol(EMI-526), g	0.5	0.5	0.5	0.5	0.5
Tap water, g	54.3	54.3	54.3	54.3	54.3
CaCl <sub>2</sub> (95%), g	18.1	18.1	18.1	18.1	18.1
CaCO <sub>3</sub> , g	35	35	35	35	35
MI Bar, g	208.9	208.9	208.9	208.9	208.9
REV DUST, % w/w	5	-	5	-	5
Class G Cem. % v/v	-	-	-	10(70g slurry)	-
Zechstein brine. % v/v	-	-	-	-	10(43 g)

3

4 The formulated fluid had a mud weight of about 11.8 ppg. Exemplary  
 5 contaminants were added to each of the fluid formulations in an amount indicated. The  
 6 initial properties of the fluid were measured and then the fluid was aged at 300 °F shown  
 7 for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured  
 8 at 120 °F. Representative data is given below:

Formulation	M	N		O		P		Q	
Fluid Properties	Aged	Initial	Aged	Initial	Aged	Initial	Aged	Initial	Aged
600 rpm Rheology	151	30	88	37	61	42	125	45	37
300 rpm Rheology	112	22	56	25	34	29	88	29	23
200 rpm Rheology	96	15	45	16	24	20	72	20	16
100 rpm Rheology	73	11	31	11	14	14	52	14	11
6 rpm Rheology	28	5	10	3	3	6	12	6	4
3 rpm Rheology	22	4	8	2	2	5	12	5	3
PV., cP	39	12	32	12	27	13	37	14	14
YP, lb/100 ft. <sup>2</sup>	73	10	24	13	7	16	51	15	9
10 s.Gel, lb/100 ft <sup>2</sup>	18	6	7	4	4	6	11	6	5
10 Min,Gel, lb/100 ft <sup>2</sup>	24	6	9	5	7	8	13	6	6
HTHP@250°F, cc/30	15.0	-	2.0	—	20.0	—	14.0	—	12.0
ES @ 120°F, Volts	329	467	258	225	165	382	287	320	258

9

Upon review of the above data, one of ordinary skill in the art should appreciate that the above-formulated fluids are useful as an invert emulsion drilling fluids.

Example 6. Drilling Fluid with 25% CaCl<sub>2</sub> Brine

A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	R	S	T	U	V
Bio Base-300, g	173.7	173.7	173.7	173.7	173.7
BENTONE 38, g	7.0	7.0	7.0	7.0	7.0
Lime, g	2	2	2	2	2
Emulphama PG20, g	10.0	10.0	10.0	10.0	10.0
VERSAWET, g	3.0	3.0	3.0	3.0	3.0
VERSA SWA, g	-	1.0	0.5	0.5	0.5
VERSAWET F, g	1.5	1.5	1.5	—	2.0
Ecotrol(EMI-526), g	0.5	0.5	0.5	0.5	0.5
Tap water, g	54.3	54.3	54.3	54.3	54.3
CaCl <sub>2</sub> (95%), g	18.1	18.1	18.1	18.1	18.1
VERSAMOD, g	—	—	—	2.0	2.0
CaCO <sub>3</sub> , g	35	35	35	35	35
MI Bar, g	208.9	208.9	208.9	208.9	208.9
REV DUST, % w/w	-	-	-	5	-
Class G Cem. % v/v	-	-	10	-	-
1.29 Zechstein brine. % v/v	-	10	-	-	-

The formulated fluid had a mud weight of about 11.8 ppg. Exemplary contaminants were added to each of the fluid formulations in an amount indicated. The initial properties of the fluid were measured and then the fluid was aged at 300 °F shown for 16 hours with rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F. Representative data is given below:

Formulation	R		S		T		U		V
Fluid Properties	Initial	Aged	Initial	Aged	Initial	Aged	Initial	Aged	Aged
600 rpm Rheology	34	66	36	36	40	82	48	88	210
300 rpm Rheology	21	41	23	22	26	49	30	52	150
200 rpm Rheology	15	28	14	12	18	35	21	39	120
100 rpm Rheology	10	17	10	8	12	22	14	25	80
6 rpm Rheology	5	3	3	2	5	5	6	8	15
3 rpm Rheology	4	2	2	1	4	3	5	6	10
PV., cP	13	25	13	14	14	33	18	36	60
Yp, lb/100 ft. <sup>2</sup>	12	16	10	8	12	16	12	16	90
10 s.Gel, lb/100 ft <sup>2</sup>	5	2	4	3	6	4	6	8	13
10 min,Gel, lb/100 ft <sup>2</sup>	5	3	5	4	7	6	8	11	19
HTHP@250°F, cc/30	--	1.8	--	5.0	--	0.2	--	15.0	24.0
ES @ 120°F, Volts	777	239	338	265	647	292	430	308	367

Upon review of the above data, one of ordinary skill in the art should appreciate that the above-formulated fluids are useful as an invert emulsion drilling fluids.

#### Example 7. Drilling Fluid with EMULPHARMA PG20 Comparison to VERSACOAT

A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	W	X
	25% CaCl <sub>2</sub> Brine	NOVA PLUS
IO C <sub>16-18</sub> , g	-	150.98
Bio Base-300, g	173.7	-
VG PLUS, g	-	4.0
BENTONE 38, g	12	-
Lime, g	2	2.0
NOVAMUL, g	-	8.0
NOVAWET, g	-	3.0
VERSACOAT, g	8.0	-
VERSAWET, g	3.0	-
Tap Water	54.3	80.97
CaCl <sub>2</sub> (97%), g	18.1	28.5
Ecotrol(EMI-526), g	0.5	-
CaCO <sub>3</sub> M, g	35	-
Ml Bar, g	208.9	226.54

The formulated fluid had a mud weight of about 11.8 ppg. The initial properties of the fluid were measured and then the fluid was aged at 300 °F shown for 16 hours with

- 1 rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F.  
 2 Representative data is given below:

	W		X
Fluid Properties	Initial	Aged	Initial
600 rpm Rheologies	36	30	57
300 rpm Rheologies	24	20	36
200 rpm Rheologies	18	12	28
100 rpm Rheologies	12	8	19
6 rpm Rheologies	5	3	7
3 rpm Rheologies	6	2	6
PV., cP	12	10	21
YP, lb/100 ft <sup>2</sup>	12	10	15
10 s. Gel, lb/100 ft <sup>2</sup>	6	4	5
10 min, Gel, lb/100 t <sup>2</sup>	8	5	7
HTHP@ 250°F, cc/30	-	6.0	-
ES @ 120°F, Volts	819	565	842

- 3  
 4 Upon review of the above data, one of ordinary skill in the art should appreciate  
 5 that the above-formulated fluids are useful as an invert emulsion drilling fluids.

6 Example 8. S/W ratio study on EMULPHARMA PG-20 With 25%CaCl<sub>2</sub> brine

- 7 A drilling fluid of the present invention was formulated to contain the following:

Fluid Formulation	Y	Z	AA	BB	CC
S/W Ratio	(60/40)	(70/30)	(90/10)	(60/40)	(70/30)
Bio Base-300, g	121.08	140.34	178.12	121.08	140.34
BENTONE 38, g	7.0	7.0	7.0	3.5	3.5
Lime, g	2	2	2	2	2
Emulpharma PG20, g	10.0	10.0	10.0	10.0	10.0
VERSAWET g	3.0	3.0	3.0	3.0	3.0
25% CaCl <sub>2</sub> brine, g	141.05	105.46	35	141.05	105.46
VERSAVERT F, ppb	1.5	1.5	1.5	1.5	1.5
Ecotrol (EMI-526), g	0.5	0.5	0.5	0.5	0.5
WERSA SWA, g	2.0	2.0	2.0	2.0	2.0
CaCO <sub>3</sub> , M, g	35	35	35	35	35
MI Bar, g	182.37	199.06	231.79	182.37	199.06

- 8  
 9 The formulated fluid had a mud weight of about 12.0 ppg. The initial properties of  
 10 the fluid were measured and then the fluid was aged at 250 °F shown for 16 hours with

- 1 rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F.  
 2 Representative data is given below:

Fluid Formulation	Y		Z	
Fluid Properties	Initial	Aged	Initial	Aged
600 rpm Rheologies	148	>300	81	232
300 rpm Rheologies	100	260	52	168
200 rpm Rheologies	83	Too thick to measure.	41	130
100 rpm Rheologies	60		30	95
6 rpm Rheologies	28		11	40
3 rpm Rheologies	23		10	35
PV., cP	48		29	72
YP, lb/100 Ft <sup>2</sup>	52		23	88
10 s. Gel, lb/100 ft <sup>2</sup>	23		12	36
10 min, Gel, lb/100 t <sup>2</sup>	26		16	50
HTHP @ 250°F, cc/30	-		-	1.0
ES @ 120°F, Volts	610	896	748	617

3

Fluid Formulation	AA		BB		CC	
Fluid Properties	Initial	Aged	Initial	Aged	Initial	Aged
600 rpm Rheologies	46	95	90	>300	62	165
300 rpm Rheologies	30	62	56	210	36	110
200 rpm Rheologies	20	50	44	165	26	84
100 rpm Rheologies	14	35	32	112	20	50
6 rpm Rheologies	6	9	12	26	7	12
3 rpm Rheologies	5	6	10	19	5	9
PV., cP	16	33	34	-	24	65
YP, lb/100 Ft <sup>2</sup>	14	29	22	-	10	45
10 s. Gel, lb/100 ft <sup>2</sup>	8	9	11	21	6	12
10 min, Gel, lb/100 t <sup>2</sup>	10	12	14	38	8	21
HTHP @ 250°F, cc/30	-	0.0	-	1.3	-	1.4
ES @ 120°F, Volts	1317	1542	409	736	490	346

4

5 Upon review of the above data, one of ordinary skill in the art should appreciate  
 6 that the above-formulated fluids are useful as an invert emulsion drilling fluids. One  
 7 would also note that the decreasing of clay concentration is followed by lower rheology  
 8 properties, formulations BB & CC.

9

1 Example 8. 70/30 S/w ratio and mud weight study on EMULPHARMA PG-20

2 Drilling fluids of the present invention were formulated to contain the following:

Fluid Formulation	DD	EE	FF	GG	HH
S/W Ratio	(90/10)	(70/30)	(70/30)	(70/30)	(70/30)
Bio Base-300, g	178.12	153.65	127.03		140.34
BENTONE 38, g	5.0	5.0	7.0	3.5	2.0
Lime, g	2	2	2	2	2
Emulpharma PG20, g	10.0	10.0	10.0	10.0	10.0
VERSAWET g	3	3	3	3	3.0
25% CaCl <sub>2</sub> brine, g	35.0	115.07	95.14	95.14	105.4
VERSAVERT F, ppb	1.5	1.5	1.5	1.5	-
Ecotrol (EMI-526), g	0.5	0.5	0.5	0.5	1.5
WERSA SWA, g	2.0	2.0	2.0	2.0	1.0
CaCO <sub>3</sub> , M, g	35	35	35	35	35
MI Bar, g	231.79	91.78	306.33	306.33	199.06

3

4 The formulated fluid had a mud weight as shown. The initial properties of the  
5 fluid were measured and then the fluid was aged at 250 °F shown for 16 hours with  
6 rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F.

7 Representative data is given below:

Fluid Formulation	DD		EE		FF	
Fluid Properties	Initial	Aged	Initial	Aged	Initial	Aged
Mud Weight, ppg	12.0	12.0	10.0	10.0	14.0	14.0
600 rpm Rheologies	41	78	53	150	130	>300
300 rpm Rheologies	25	50	35	100	86	210
200 rpm Rheologies	16	38	25	92	69	182
100 rpm Rheologies	11	25	18	60	50	135
6 rpm Rheologies	5	6	7	22	22	63
3 rpm Rheologies	4	4	6	16	20	55
PV., cP	16	28	18	50	44	-
YP, lb/100 Ft <sup>2</sup>	9	22	17	50	42	-
10 s. Gel, lb/100 ft <sup>2</sup>	6	6	7	19	20	60
10 min, Gel, lb/100 t <sup>2</sup>	7	11	10	29	22	68
HTHP @ 250°F, cc/30	-	1.5	-	0.5	-	-
ES @ 120°F, Volts	1309	1115	565	888	822	895

8

Fluid Formulation	GG		HH	
Fluid Properties	Initial	Aged	Initial	Aged
Mud Weight, ppg	14.0	14.0	12.0	12.0
600 rpm Rheologies	82	188	72	96
300 rpm Rheologies	52	120	50	56
200 rpm Rheologies	40	95	40	44
100 rpm Rheologies	28	62	30	27
6 rpm Rheologies	10	19	10	7
3 rpm Rheologies	9	13	8	5
PV., cP	30	68	22	40
YP, lb/100 Ft <sup>2</sup>	22	52	28	16
10 s. Gel, lb/100 ft <sup>2</sup>	10	19	8	9
10 min, Gel, lb/100 t <sup>2</sup>	10	25	11	15
HTHP @ 250°F, cc/30	-	4.4	-	3.0
ES @ 120°F, Volts	670	708	641	847

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Upon review of the above data, one of ordinary skill in the art should appreciate that the above-formulated fluids are useful as an invert emulsion drilling fluids. It should also be noted that decreasing the concentration of the clay lowered rheology, formulation GG.

Example 9. 70/30 & 80/20 SWR with 25% CaCl<sub>2</sub> Brine

Drilling fluids of the present invention were formulated to contain the following:

Fluid Formulation	II	JJ
S/W Ratio	(70/30)	(80/20)
Bio Base-300, g	140.3	173.0
BENTONE 38, g	2.0	12.0
Lime, g	2	2
GS-17 29	10.0	10.0
VERSAWET g	3	3
25% CaCl <sub>2</sub> brine, g	105.4	72.4
VERSAVERT F, ppb	1.5	1.5
Ecotrol (EMI-526), g	-	0.5
VERSA SWA, g	1.0	-
CaCO <sub>3</sub> , M, g	35	35
MI Bar, g	199.06	208.9

9

1 The formulated fluid had a mud weight as shown. The initial properties of the  
2 fluid were measured and then the fluid was aged at 250 °F shown for 16 hours with  
3 rolling. Rheology of the initial fluid and the aged fluid were measured at 120 °F.  
4 Representative data is given below:

Fluid Formulation	II		JJ	
Fluid Properties	Initial	Aged	Initial	Aged
Mud Weight, ppg	12.0	12.0	10.0	10.0
600 rpm Rheologies	69	100	120	120
300 rpm Rheologies	47	65	34	82
200 rpm Rheologies	40	51	24	67
100 rpm Rheologies	28	36	15	47
6 rpm Rheologies	7	20	6	22
3 rpm Rheologies	5	18	5	20
PV., cP	22	35	20	43
YP, lb/100 Ft <sup>2</sup>	25	30	14	39
10 s. Gel, lb/100 ft <sup>2</sup>	5	21	6	27
10 min, Gel, lb/100 t <sup>2</sup>	8	29	10	35
HTHP @ 250°F, cc/30	-	7.0	-	1.2
ES @ 120°F, Volts	347	681	677	1617

5  
6 Upon review of the above data, one of ordinary skill in the art should appreciate  
7 that the above-formulated fluids are useful as an invert emulsion drilling fluids. It should  
8 also be noted that decreasing the concentration of the clay lowered rheology, formulation  
9 GG.

10 In view of the above disclosure, one of ordinary skill in the art should understand  
11 and appreciate that one illustrative embodiment of the present invention includes an  
12 invert emulsion drilling fluid that is formulated to include: an oleaginous continuous  
13 phase, a non-oleaginous discontinuous phase a surfactant that is a fatty acid ester of  
14 diglycerol or triglycerol, and a weighting agent. In one such illustrative embodiment, the  
15 surfactant is a di-fatty acid ester of diglycerol in which the fatty acid has the formula  
16 RCO<sub>2</sub>H and the R is an alkyl or akenyl having 10 to 20 carbon atoms. Alternatively, the  
17 surfactant is a di-fatty acid ester of triglycerol in which the fatty acid has the formula  
18 RCO<sub>2</sub>H and the R is an alkyl or akenyl having 10 to 20 carbon atoms. More preferably  
19 the surfactant is selected from polyglyceryl-2 diisostearate or polyglyceryl-3 diisostearate



1 or mixtures and combinations of these. One of skill in the art should appreciate that the  
 2 oleaginous fluid may be selected from a variety of suitable fluids known in the art,  
 3 including diesel oil, mineral oil, synthetic oil, ester oils, glycerides of fatty acids,  
 4 aliphatic esters, aliphatic ethers, aliphatic acetals, or other such hydrocarbons and  
 5 combinations and mixtures of these and similar fluids. In a similar manner, the non-  
 6 oleaginous phase may be selected from a wide range of suitable fluids known in the art  
 7 including fresh water, sea water, brine, aqueous solutions containing water soluble  
 8 organic salts, water soluble alcohols or water soluble glycols or combinations and  
 9 mixtures of these and similar fluids. The weighting agent component of such an  
 10 illustrative drilling fluid can be either a water soluble weighting agent or a water  
 11 insoluble weighting agent or combinations and mixtures of these two. In one illustrative  
 12 embodiment, the water insoluble weighting agent is selected from barite, calcite, mullite,  
 13 gallena, manganese oxides, iron oxides, or combinations and mixtures of these and  
 14 similar solid materials used to weight drilling fluids. In another illustrative embodiment,  
 15 the water soluble weighting agent is selected from water soluble salts of zinc, iron,  
 16 barium, calcium or combinations and mixtures of these in aqueous solutions used to add  
 17 weight to drilling fluids.

18 It should further be appreciated that another illustrative embodiment of the present  
 19 invention includes an invert emulsion drilling fluid formulated to include: an oleaginous  
 20 continuous phase, a non-oleaginous discontinuous phase, a biodegradable surfactant  
 21 including a di-fatty acid ester of diglycerol, and a weighting agent. In such instances, the  
 22 fatty acid preferably has the formula  $\text{RCO}_2\text{H}$  in which R is an alkyl or akenyl having 10  
 23 to 20 carbon atoms. More preferably the di-fatty acid ester of diglycerol is a  
 24 polyglyceryl-2 diisostearate.

25 Yet another illustrative embodiment of the present invention includes an invert  
 26 emulsion drilling fluid that includes: an oleaginous continuous phase, a non-oleaginous  
 27 discontinuous phase, a biodegradable surfactant including a di-fatty acid ester of  
 28 triglycerol in which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and R is an alkyl or akenyl  
 29 having 10 to 20 carbon atoms, and a weighting agent. It is preferred that the di-fatty acid  
 30 ester of triglycerol is polyglyceryl-3 diisostearate.

1 It will also be appreciated by one of ordinary skill in the art that a present  
2 illustrative embodiment of the present invention includes a method of formulating an  
3 invert emulsion drilling fluid so as to exhibit the characteristics of the above described  
4 fluids. One such illustrative method, includes mixing an oleaginous fluid, a non-  
5 oleaginous fluid, a biodegradable surfactant and a weighting agent to form and invert  
6 emulsion. The biodegradable surfactant includes a fatty acid ester of diglycerol or  
7 triglycerol in amounts sufficient to form an invert emulsion in which the oleaginous fluid  
8 is the continuous phase and the non-oleaginous fluid is the discontinuous phase. In one  
9 preferred illustrative embodiment the fatty acid ester is a di-fatty acid ester of diglycerol  
10 in which fatty acid has the formula  $RCO_2H$  and R is an alkyl or akenyl having 10 to 20  
11 carbon atoms. In another preferred illustrative embodiment, a di-fatty acid ester of  
12 triglycerol is utilized in which the fatty acid has the formula  $RCO_2H$  and R is an alkyl or  
13 akenyl having 10 to 20 carbon atoms. The oleaginous fluid is preferably selected from  
14 diesel oil, mineral oil, synthetic oil, ester oils, glycerides of fatty acids, aliphatic esters,  
15 aliphatic ethers, aliphatic acetals, or other such hydrocarbons and combinations and  
16 mixtures of these and similar fluids. Similarly, the non-oleaginous phase is preferably  
17 selected from fresh water, sea water, brine, aqueous solutions containing water soluble  
18 organic salts, water soluble alcohols or water soluble glycols or combinations and  
19 mixtures of these and similar fluids. In one preferred illustrative embodiment, the  
20 weighting agent is either a water soluble weighting agent or a water insoluble weighting  
21 agent or combinations and mixtures of the two. In such cases, the water insoluble  
22 weighting agent is preferably barite, calcite, mullite, gallena, manganese oxides, iron  
23 oxides, or combinations and mixtures of these and similar weight materials while the  
24 water soluble weighting agent is preferably selected from water soluble salts of zinc, iron,  
25 barium, calcium or combinations and mixtures of these and similar materials.

26 It should also be appreciated that the present invention encompasses a method of  
27 drilling a subterranean hole with the invert emulsion drilling fluids as described above,  
28 such an illustrative method includes: mixing an oleaginous fluid, a non-oleaginous fluid,  
29 a biodegradable surfactant, and a weighting agent to form an invert emulsion, and drilling  
30 said subterranean hole using said invert emulsion as the drilling fluid. It is preferred that

1 the biodegradable surfactant is a fatty acid ester of diglycerol or triglycerol that is present  
 2 in amounts sufficient to form an invert emulsion in which the oleaginous fluid is the  
 3 continuous phase and the non-oleaginous fluid is the discontinuous phase. In a more  
 4 preferred embodiment, the fatty acid ester of diglycerol or triglycerol is a di-fatty acid  
 5 ester of diglycerol in which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and the R is an alkyl or  
 6 akenyl having 10 to 20 carbon atoms. Alternatively, the fatty acid ester of diglycerol or  
 7 triglycerol may be a di-fatty acid ester of triglycerol in which fatty acid has the formula  
 8  $\text{RCO}_2\text{H}$  and the R is an alkyl or akenyl having 10 to 20 carbon atoms. As disclosed  
 9 above, the oleaginous fluid is preferably selected from diesel oil, mineral oil, synthetic  
 10 oil, ester oils, glycerides of fatty acids, aliphatic esters, aliphatic ethers, aliphatic acetals,  
 11 or other such hydrocarbons and combinations and mixtures of these and similar fluids.  
 12 The non-oleaginous phase is preferably selected from fresh water, sea water, brine,  
 13 aqueous solutions containing water soluble organic salts, water soluble alcohols or water  
 14 soluble glycols or combinations and mixtures of these and similar fluids. The weighting  
 15 agent can be a water-soluble weighting agent or a water insoluble weighting agent or  
 16 combinations of the two. Preferably the water insoluble weighting agent is selected from  
 17 barite, calcite, mullite, gallena, manganese oxides, iron oxides, or combinations and  
 18 mixtures of these and similar weighting agents. While the water soluble weighting agent  
 19 is selected from water soluble salts of zinc, iron, barium, calcium or combinations and  
 20 mixtures of these and similar weighting agents.

21 Also encompassed is a method of drilling a subterranean well with an invert  
 22 emulsion drilling fluid, said method comprising: mixing an oleaginous fluid, a non-  
 23 oleaginous fluid, a biodegradable surfactant, and a weighting agent to form an invert  
 24 emulsion, circulating said invert emulsion within said subterranean well and drilling said  
 25 subterranean well using said invert emulsion as the drilling fluid. In such an illustrative  
 26 embodiment, the biodegradable surfactant includes a fatty acid ester of diglycerol, in  
 27 which the fatty acid has the formula  $\text{RCO}_2\text{H}$  and R is an alkyl or akenyl having 10 to 20  
 28 carbon atoms. The biodegradable surfactant is in amounts sufficient to form an invert  
 29 emulsion in which the oleaginous fluid is the continuous phase and the non-oleaginous  
 30 fluid is the discontinuous phase. It is preferred that the fatty acid ester of diglycerol is a

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1 di fatty acid ester and more preferably the fatty acid ester of diglycerol is polyglyceryl-2  
2 diisostearate.

3 Another illustrative embodiment includes a method of drilling a subterranean well  
4 with an invert emulsion drilling fluid, in which the method includes: mixing an  
5 oleaginous fluid, a non-oleaginous fluid, a biodegradable surfactant, and a weighting  
6 agent to form an invert emulsion, circulating said invert emulsion within said  
7 subterranean well and drilling said subterranean well using said invert emulsion as the  
8 drilling fluid. As part of the illustrative method, the biodegradable surfactant includes a  
9 fatty acid ester of triglycerol having the formula  $\text{RCO}_2\text{H}$  in which the R is an alkyl or  
10 akenyl having 10 to 20 carbon atoms. The biodegradable surfactant is in amounts  
11 sufficient to form an invert emulsion in which the oleaginous fluid is the continuous  
12 phase and the non-oleaginous fluid is the discontinuous phase. It is preferred that the  
13 fatty acid ester of triglycerol is a di-fatty acid ester and more preferably the fatty acid  
14 ester of triglycerol is polyglyceryl-3 diisostearate.

15 While the apparatus, compositions and methods of this invention have been  
16 described in terms of preferred or illustrative embodiments, it will be apparent to those of  
17 skill in the art that variations may be applied to the process described herein without  
18 departing from the concept and scope of the invention. All such similar substitutes and  
19 modifications apparent to those skilled in the art are deemed to be within the scope and  
20 concept of the invention as it is set out in the following claims.